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SURFACE TENSION AT THE INTERFACE BETWEEN CERTAIN LIQUIDS AND VAPORS.

BY ARTHUR L. CLARK.

Presented by A. G. Webster, May 10, 1905. Received Oct. 11, 1905.

ALL determinations of the capillary constants of liquids are made necessarily with the liquid used in contact with its saturated vapor, a gas, or another liquid. The constant for a free liquid surface, i. e., one not in contact with any other substance, cannot be determined, although the value for a liquid near its freezing-point and in contact with its own vapor cannot be far from the true value. It is true, however, that almost all methods for the determination of the constant measure the tension at the line of contact with a solid and not on the undisturbed surface.

The values of the constant for various liquids have been determined by a large number of observers.* Quincke † has determined the constant for the interface of two different liquids, and Kundt ‡ for liquids in contact with gases under pressure. Both of these observers worked at room temperatures. Quincke found that $a_1 < a_2 + a_{12}$, because of solution of the two liquids in each other. Kundt found that the surface tension between a liquid and a gas decreases rapidly with increasing pressure. Wroblewski § showed that this effect was due to solution of the gas in the liquid. Since the surface tension of mixtures obeys approximately the centre of mass law, we can readily see that we must have a very great lowering of the capillary constant, when one liquid is replaced by a gas whose surface tension is practically zero.

A very large number of experimenters || have investigated the effect of raising the temperature of a substance upon its capillary constant, and have found that, in every case, a rise in temperature is accompanied by a

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* See Winkelmann, Handbuch der Physik, Vol. 1, page 497, for a very complete bibliography of the subject.

† Quincke, Pogg. Ann., **139**, 1 (1870).

‡ Kundt, Wied. Ann., **12**, 538 (1881).

§ Wroblewski, Compt. Rend., **95**, 284 (1882).

|| See Winkelmann, Handbuch der Physik, loc. cit.

decrease in the constant. Kasterine,* and Ramsay and Shields † have pushed the observations to the critical point and have shown that the constant becomes zero at this point. This had been studied qualitatively many times, but the above-mentioned observers have carried out quantitative investigations.

The vanishing of the capillary constant of the interface noticed by these observers is to be attributed not to the vanishing of the constant of the liquid, but to the fact that the values for the liquid and vapor have approached equality, causing the boundary surface to disappear.

The capillary constant of the boundary between two liquids at high temperatures and pressures, and between a liquid and the saturated vapor of another liquid has not been investigated. The following research is an attempt to supply to some slight extent these missing data. It will be readily seen that the choice of liquids is limited, if the experiments are to be pushed to temperatures much above the room temperatures. The substances should be as nearly insoluble as possible in each other, should not act upon each other chemically; the vapor density of one, at least, should be very small in experiments on vapors. As yet little more than a beginning has been made, as the larger part of the available time has been spent in devising and testing the apparatus and methods.

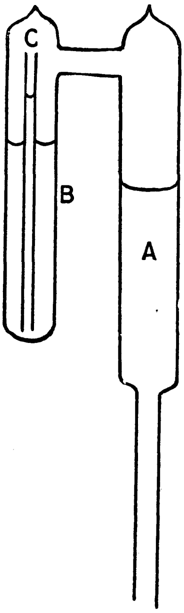

FIGURE 1.

THEORY OF EXPERIMENTS.

The method of experimenting on the surface between a liquid and the saturated vapor of another liquid will be described first. The substances were placed in a glass tube of the general appearance shown in Figure 1.

The part *A* contains the liquid to be vaporized, the part *B*, the liquid whose surface is to be studied. *C* is a small capillary tube suspended inside *B*. The surface tension is found by measuring the height of the meniscus in the capillary above that in the large tube, the diameters of the two tubes, and the angle of contact. Then

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* Kasterine, Journ. de Phys. (3), **2**, 529 (1893).

† Ramsay and Shields, Phil. Trans., **184**, 647 (1893).

$$a = \frac{g\,H(d - d')}{2\cos\omega\left(\frac{1}{r_1} - \frac{1}{r_3 - r_2}\right)}\ *$$

where a is the surface tension, H the height of the meniscus, d and d' the densities of the liquid and vapor respectively, ω the contact angle, and r_1, r_2, and r_3, the inner and outer radii of the capillary tube and the inner radius of the containing tube respectively. The angle of contact was found by measuring the depth of the meniscus and the radius of the tube. Then considering the meniscus a portion of a sphere,

$$\omega = \frac{\pi}{2} - 2\tan^{-1}\frac{h'}{r_1},$$

h' being the depth of the meniscus. This method of determining ω is not satisfactory, for it assumes a spherical meniscus, which shape is of course realized less and less as we near the wall of the tube. It also assumes a perfectly circular cross-section. A better method has been projected, but not yet tested.

The capillary tube method of measurement of surface tension leaves much to be desired when applied under such severe conditions as in the present work.

The tube used in the liquid experiments was not of the complicated form used in the vapor tests, but both liquids were placed in the same tube. The measurements for the determination of a were made exactly as just described.

These tubes were placed in an electric heater controlled by an automatic thermostat, and the constant observed for different temperatures. The lower part of the experimental tube was connected with a manometer. In this way the capillary constant and pressure could be deter-

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* The system being in equilibrium, the pressures inside and outside the capillary tube at the level of the meniscus outside are equal.

So

$$\frac{2\pi r_1 T\cos\omega - \pi r_1^2 g\,d_1}{\pi r_1^2} = \frac{2\pi(r_3 + r_2)\,T\cos\omega - \pi(r_3^2 - r_2^2)\,g\,H\,d_2}{\pi(r_3^2 - r_2^2)}$$

or

$$2\,T\cos\omega\left(\frac{1}{r_1} - \frac{1}{r_3 - r_2}\right) = g\,H\,(d_1 - d_2)$$

whence

$$T = \frac{g\,H\,(d_1 - d_2)}{2\cos\omega\left(\frac{1}{r_1} - \frac{1}{r_3 - r_2}\right)}$$

mined for any temperature at will. The manometer also served as a criterion of constancy of temperature.

DESCRIPTION OF APPARATUS.

Heating Apparatus and Thermostat.

The heating is done electrically and the temperature is controlled by a self-regulating thermostat. As a large amount of work has been planned requiring an automatically controlled thermostat working over a wide range of temperature, it was decided to build it once for all; and, though for a large amount of work a simpler controller might be used, the ease of manipulation and certainty of operation repaid for the extra trouble in building.

The thermostat is a modification of the one used by Griffiths * in his work on "The Value of the Mechanical Equivalent of Heat."

It consists of a cast-iron box *A* (Figure 2), the walls of which are hollow and filled with mercury. The expansion of the mercury closes the relay circuit, which controls the heating current. The construction of this box was attended with serious difficulty because, on account of the openings for fan shafts, windows, and experimental tubes, it was deemed best to make the box in one casting. The walls are hollow except where the openings occur, where they are solid for a space of about 1 cm. about the openings. I am indebted to Mr. L. S. Burbank for the method of making the patterns for this casting. The hollow walls and the interior of the box itself were cored, the pattern being one solid piece.

The top of the box was planed smooth, and then ground by rubbing on a large sheet of plate glass covered with powdered emery and oil. The cover of the mercury chamber was also planed and ground, and screwed on tightly with just enough silicate of soda to ensure perfect tightness. Finally the removable cover was fitted on. Then the holes for the windows and fan shafts in the sides and for the experimental tubes in the bottom were drilled. These holes were of course bored through the solid places in the walls. The dimensions of the box are 15 × 15 × 15 cm. outside. The walls are 6 cm. thick, the hollow space being the same size. Both the cover to the mercury chamber and the removable cover are .6 cm. thick. The mercury chamber contains 420 c.c. There are two openings in the cover to this chamber, one for the overflow to the regulator and the other for convenience in filling, which later is closed with a steel plug. The chamber was filled by heating to about 250° and pumping out the air at one opening and allowing clean dry mercury to run in at the other. In this way all air and moisture could be removed from the mercury and the chamber. When full the box was allowed to cool while still connected with the mercury supply.

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* Griffiths, Phil. Trans., **184**, 361 (1893).

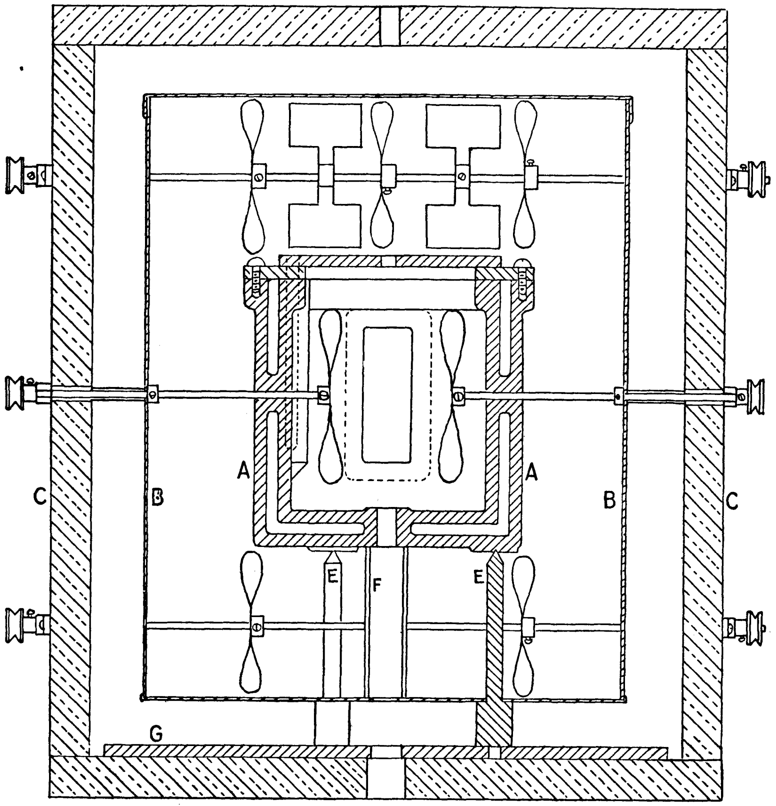

FIGURE 2.

Then the second hole in the cover was closed by a steel plug securely screwed in.

The windows are of glass held in place by springs of heavy steel wire wound horizontally around the box. On the bottom of the box are three bosses provided with conical hole, groove, and plane respectively for the support of the box which rests on three pillars to be described.

At two opposite points on the inside wall of the box are projections into which vertical holes are bored for the insertion of thermometers. These holes are 8 cm. deep and .75 cm. in diameter, and are filled with mercury which thus surrounds the thermometers. In the covers are holes exactly coinciding with the thermometer holes.

As already stated, the heating is done electrically. This is accomplished by means of coils of German silver wire, .035 cm. in diameter, which surround the iron box on five sides. These coils are suspended on supports made of glass tubing fastened to the sides of the enclosing box.

This enclosing box *B* (Figure 2) is made of sheet copper, the dimensions of which are 23 × 23 × 32 cm. There are holes for windows, thermometers, shafts, and tubes corresponding to the holes in the iron box.

The copper box is in turn enclosed in a wooden box or case, the space between the copper and wood being packed with magnesia.

The external dimensions of the wooden case are 35 × 35 × 43 cm. Where the fan shafts pass through the magnesia, metal tubes were inserted and the magnesia was moistened with water so that when hard the tubes were held in position. These tubes serve to prevent the magnesia from falling upon the shafts.

It will readily be seen that, on account of the numerous holes in the iron box as well as in the enclosing box, a liquid bath for heating is out of the question. There is no doubt that a liquid may be stirred more easily than air; but after all efficient stirring means the rapid and constant moving of the heated substance from the source to the body under experiment. In the heater used, this is accomplished by a system of sixteen fans of sheet iron, carried on six shafts which are run at high speed by an electric motor. These fans are about 7.5 cm. in diameter and create a strong circulation in the heated space around the iron box. There are two fans inside the iron box to ensure uniformity of temperature. This is necessary on account of the breaks in the continuity of the iron box. The shafts for the fans are made of steel rod about .3 cm. in diameter and run in bearings screwed to the outside of the wooden case. The shafts for the inner fans have their inner bearings in the iron box itself, and these bearings are oiled by means of oil tubes which project through the wooden case.

In the bottom of the case was screwed a heavy iron plate *G*, in which were fastened the steel pillars *E*, which support the iron and copper boxes. These pillars are 16 cm. long and are .6 cm. in diameter for a distance of 7 cm. from the conical end. Then they are 1.2 cm. in diameter for the remainder of the length. The copper box rests on the shoulders thus formed, while the iron box rests on the points. Thus, whenever it is necessary to take down the apparatus, it may be put together again in perfect alignment with very little trouble. The whole system, which weighs about 40 kg., is slung from the ceiling by rope and pulleys. The case is supported by heavy iron straps and is also provided with large screw-eyes which slide on two upright steel rods, securely fastened to the work-table. This allows vertical adjustment and prevents swaying and tipping. *F* is a porcelain tube inserted in the heated space to protect the experimental tube from becoming heated too rapidly, since otherwise the lower part of the latter, being filled with mercury, would be unduly heated in the warming-up stages and cause distillation of the liquid in the tube above.

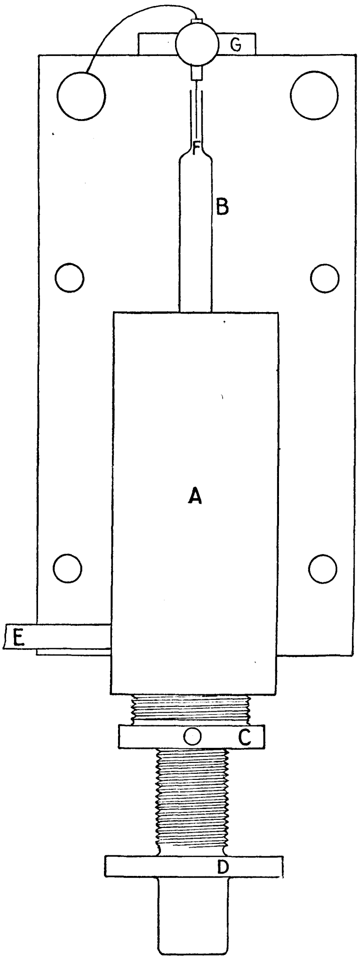

FIGURE 3.

The resistance of the heater is 10 ohms, and is used on the 110-volt alternating lighting circuit. This, though unsteady through a small range of voltage, answers very well, since the changes of temperature in the heater take place slowly.

It remains now to describe the automatic part of the regulator. Since the thermostat was designed for temperatures between room temperature and 300° C., an overflow chamber of adjustable capacity is necessary. This is shown in Figure 3.

A cast-iron cylinder *A*, with an opening for a glass tube *B* in the upper end, and a stuffing-box *C* with screw *D* in the lower end, is screwed firmly to the front of the wooden case. The side tube at *E* communicates with the mercury chamber of the iron box of the heater. The glass tube at *B* is .2 cm. in diameter at the upper part, the lower part being much larger.

A platinum wire *F* is held in place by a screw in the hard rubber block *G*. The mercury rising by the expansion completes the relay circuit at *F*, and the heating current is either cut off or reduced until the apparatus cools off again. The screw in the lower part of the chamber enables the capacity to be suited to the temperature desired. The total capacity of this chamber is about 20 c.c., the expansion of the mercury at 300° being about 18 c.c. The screw is three-fourths of an inch in diameter and the pitch is sixteen threads to the inch. The glass tube is cemented in with silicate of soda and the screw is packed with rubber washers held between leather ones. The tube communicating with the iron box is of steel about .5 cm. in diameter. A rise of temperature of one degree causes an ascension in the glass tube of about 2 cm. With the regulator cutting off the entire current, the regulation is within

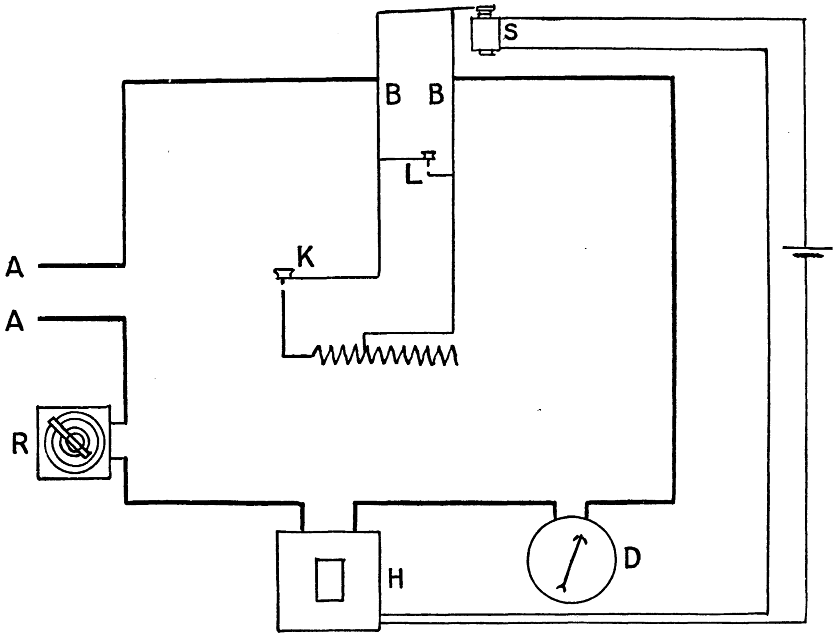

FIGURE 4.

$\frac{1}{10}$° C. at a temperature as high as 200°. By cutting off only a small portion of the current the regulation to within $\frac{1}{100}$° is very simple.

The arrangement of the circuit is shown in Figure 4. *A A* are the mains, *R* a large resistance adjustable through a wide range, *H* is the heater, *D* the ammeter. The gap *BB* is bridged over either by the relay *S* or the key *L*. When the relay is operated by the thermostat, the circuit is broken and the current sent through the variable resistance provided the key *K* is closed, otherwise the circuit remains open.

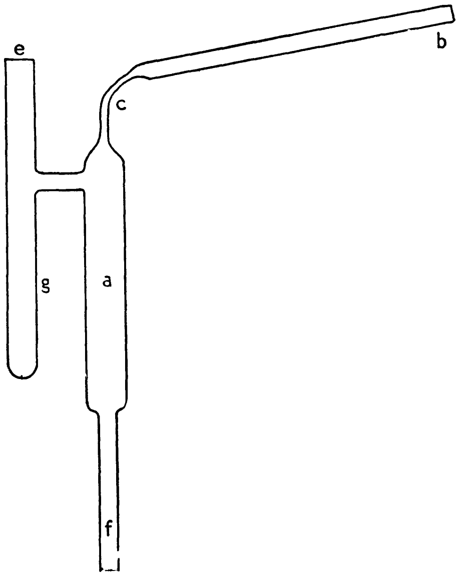

Figure 5.

Experimental Tubes.

Considerable difficulty was experienced in making a style of tube which would do the work required of it, be easy to insert in the apparatus and easy to fill. After many months of trial and failure and almost innumerable accidents, the form shown in Figure 1 was adopted. Since the pressures are considerable, the glass tubing must be selected with great care. The tubing finally adopted was obtained from the Bausch & Lomb Optical Company, and with its purchase ended a great many difficulties.

The tubing was carefully washed with aqua regia and caustic potash and finally with distilled water, and dried with a current of air.

The tubes are made in the form shown in Figure 5, the lower end being as in Figure 8.

The part *a* is about 6 cm. long, *e* is left open for the insertion of the capillary. This capillary is held in place by a platinum clip shown developed in Figure 7. The end *b* is left open for the attachment of the distilling apparatus; *c* is drawn out, being left large enough for safe handling. After the insertion of the capillary, care being taken to centre it accurately in the tube *g*, the part *d* is drawn down as shown in Figure 6. The heavy liquid is now placed in the tube *g* and the end *e* bent over for attachment to the pump. The lower end of the tube as well as the method of holding it in the steel chamber is shown in Figure 8.

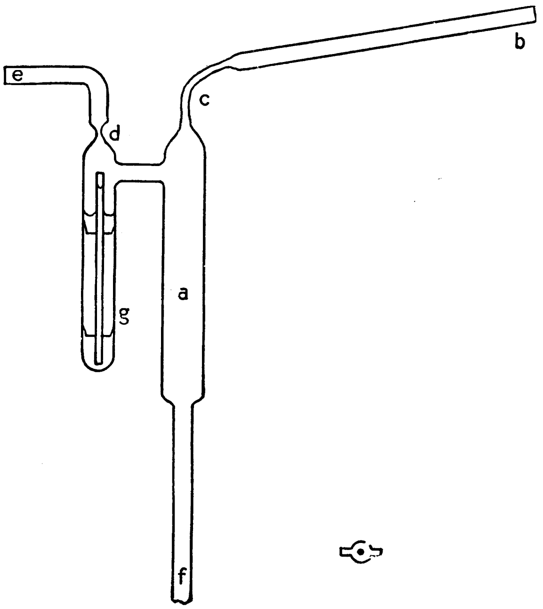

Figure 6.

Figure 7.

L is a large steel chamber (capacity 20 cm.) containing pure mercury; *K* is a stuffing-box screwed down on the rubber packing *g*. The glass tube *f* is inserted in the heater down through the hole in the bottom. The piece *J* is slipped on, then the steel washer *e*, and finally a rubber stopper *c*. By slightly moistening the tube with glycerine, the stopper may be worked over the enlargement *M*. Then *J* is screwed down and the stopper entering the narrow place at *d*, effectually closes the opening. The expanded part *M* prevents the tube from being pressed up through the stopper. This form of joint is perfectly tight up to 100 atmospheres and probably would be at much higher pressures. The joint is very flexible and the tube may be rotated very easily. After the insertion of the tube, the heater is lowered as far as possible, the tube *b* is sealed on to the retort containing the liquid to be distilled in. There is a stop-cock in this tube. The tube *e* (Figure 6) is attached to the air-pump also through a cock. Next the narrow parts in the two tubes are drawn out very small and when cool the air-pump is started and the lower part of the tube is heated. The mercury in the steel chamber is allowed to rise very slowly, being kept very hot to drive out air and moisture. This is continued until the part *a* is partly filled. The tube *a* is now allowed to cool. The air-pump still operating, *b* is gradually heated with a coil of wire to ensure the driving out of any air that may have entered during the filling. Now *a* is kept cool with ice, and *b* hot with the electric current, and the liquid distilled over from the retort. The first distillate is boiled away to carry off any air still remaining. Then the liquid is distilled over and when the proper amount is obtained the cock to the still is closed, the narrow part sealed off, then the other tube sealed off, and the tube is complete. The tube is now rotated until in the best position for observation, the heater is raised to the proper height and the cover put on, thermometers inserted, and the experiment begun.

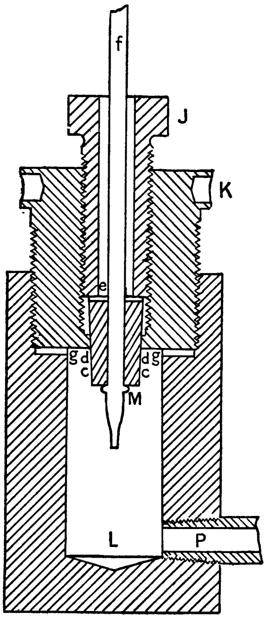

FIGURE 8.

MANOMETER.

The manometer is patterned after Amagat's and was made from drawings loaned by Professor Barus of Brown University, the sizes of the pistons being changed to suit the work in hand. The large piston is 5 cm. in diameter and the small one about 1 cm., the reduction factor being 24.42. A complete description of this manometer is given in

Amagat's paper,* and in the translation by Barus in the book edited by him entitled "The Laws of Gases," p. 55. A few modifications deserve mention, — the change of piston areas, and the substitution of light engine oil in place of castor oil, and of a heavy cylinder oil in place of molasses, this substitution being made according to a suggestion of Professor Barus'. Figure 9 shows the manometer used in this work.

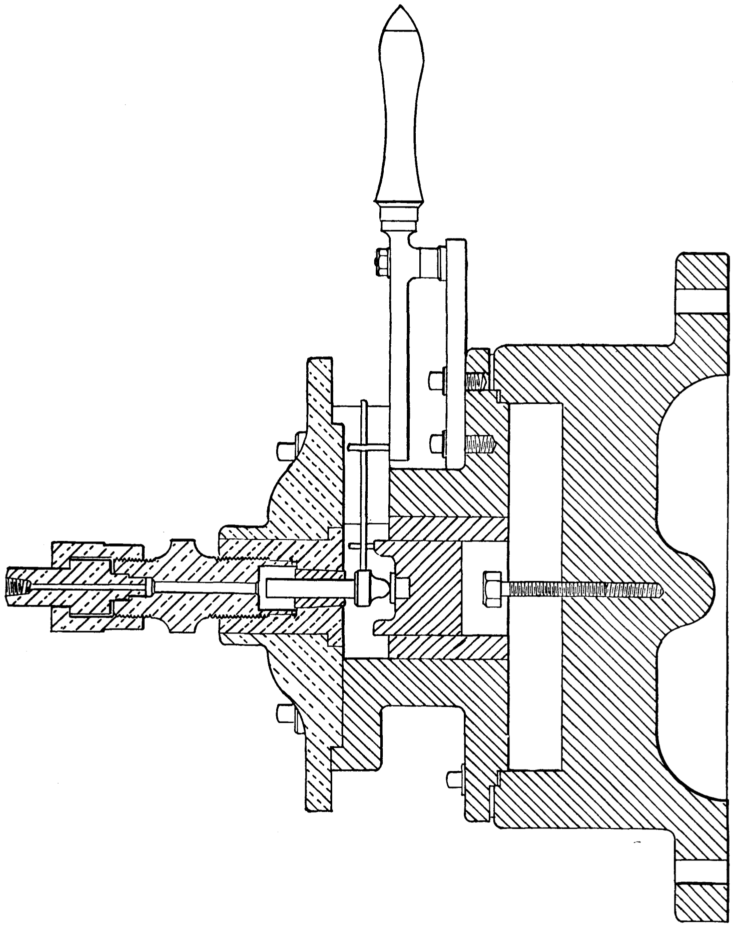

Figure 9.

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* Amagat, Annales de Chimie et de Physique, **6**, 19 (1893).

The pistons were made of tool steel hardened and ground as were the cylinders in which they move. The fit is exceedingly good, there being very little leakage of oil and scarcely any friction. It was feared that the manometer would not give accurate results for pressures below ten atmospheres, but the results are surprisingly good. It was compared with an open mercury manometer and the error for readings as low as one atmosphere was less than 1 per cent.

The glass tube in which the pressures are read is 4 mm. in diameter internally, and the scale is made of ordinary laboratory wooden meter sticks. A displacement of one millimeter represents about 2.5 cm. on an open manometer. The pump of the manometer is smaller than that described by Amagat, and is used merely to control the position of the pistons. The vertical motion of the pistons is aided by a twist given to them by means of a lever, as described by Amagat. The manometer has given the best of satisfaction and has proved itself a very valuable adjunct to the laboratory. I am indebted to Professor Barus for the drawings, the castings, and for many valuable suggestions.

Since there are unavoidable minute leaks, and since when the manometer operates there is an appreciable motion of the pistons and necessarily an increase of volume in the experimental tubes, it is necessary to provide some means of compensation. This is accomplished by a screw forced into a steel oil chamber which is connected with the mercury chamber under the heater (Figure 8) and with the manometer. This oil chamber is simply a piece of steel shafting bored out to a diameter of seven-eighths of an inch, and a steel screw three-fourths of an inch, forced in by a hand wheel ten inches in diameter. The pitch of the screw is sixteen, and the thread is packed with leather washers which had been previously boiled in marine glue. Professor Barus has shown the efficacy of marine glue for such purposes. The packing thus formed is screwed down with the gland of the stuffing-box.

Between the compressor just described and the mercury chamber of Figure 8 is another reservoir for mercury. This is simply a chamber filled with mercury and oil, connecting at the bottom with the mercury reservoir of Figure 8 and at the top with the compressor. This obviates soiling the mercury which comes in contact with the glass experimental tube, and the mercury chamber, too, is kept clean.

Between the two mercury chambers and also between the compressor and the manometer are steel cocks which deserve mention. These are made as shown in Figure 10. The especial feature is the hardened steel conical stem which rotates on the stem proper. This cone is ground to fit the seat, which is relieved at the tip. These cocks always close tightly and do not break down at critical times as do such cocks when seated with some soft metal like tin or lead.

All joints, whether containing mercury or oil, are heated, smeared with marine glue, and screwed together hot, and never leak.

MICROSCOPE.

The observing is done with a micrometer microscope whose working focal length is 10 cm. It is carried on a micrometer slide so that the stationary wire of the eyepiece may be kept on the surface of the liquid in the outer part of the experimental tube, one observation only being required to measure the capillary height. One division of the eyepiece micrometer corresponds to .005 mm. The whole system is supported on a rigid iron base, whose height is adjustable. The thermometers used were made by Baudin, readings being taken to $\frac{1}{10}°$.

METHOD OF EXPERIMENTATION.

The microscope is focused on the tube and the stationary wire set on the base level, the movable one on the meniscus, and several readings made on each of the instruments. The current is turned on and the regulator set for the next higher temperature. As the temperature rises, there is always a slight displacement of the liquid in the experimental tube which is easily compensated by the compressor. It is desirable that the volume should be kept as nearly constant as possible, since any considerable change may produce decided changes in temperature, especially at high temperatures. After the temperature is steady, as shown by the thermometer, readings were taken on the manometer to ensure constancy of temperature.

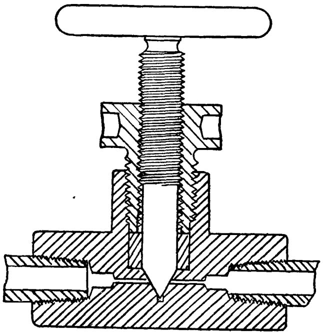

FIGURE 10.

The entire run with one tube occupies from ten to fifteen hours when there are no accidents.

The density of the heavier liquids was determined with a pyknometer, being treated in the heater at various temperatures and then weighed with the contents.

The following figures show the results for glycerine and olive oil:

Glycerine.		Olive Oil.	
Temp.	Density.	Temp.	Density.
31.3°	1.255	21°	.9127
100°	1.207	43°	.8986
150°	1.167	90.4°	.8654
190°	1.134	134.7°	.8372
235°	1.089	178.2°	.8081
		225.5°	.7790

Curves shown in Figure 11 were plotted and the densities used in calculation taken from these.

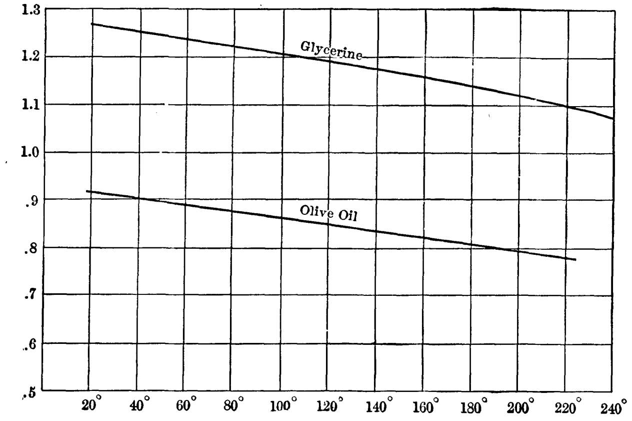

FIGURE 11.

The values of vapor densities of lighter liquids were taken from results obtained by other observers, and the curves of Figure 12 plotted. These particular figures are from Ramsay and Young.*

The diameters of the capillary tubes were determined by breaking and measuring with microscope.

Thus far the liquids observed divide themselves into two groups: 1st, those in which the vapor of the vaporized liquid condenses on the other liquid at a temperature higher than the temperature of the saturated vapor, and 2d, those in which this condensation temperature is lower than the saturation temperature. Cantor † has shown that whether or not a vapor spreads out on another liquid depends on the values of the surface tension of the liquid, of the condensed vapor, and of the interface; i. e., when the liquid from the condensed vapor wets or spreads out over the second liquid, the vapor will be condensed even when the temperature is above the saturation temperature. In order to keep such a surface dry, the temperature must be maintained several degrees higher than the saturation temperature. This makes observation with such a pair of substances very difficult. In the earlier parts of the experiment several months were spent determining whether this condensation was due to the above-mentioned phenomenon or to unequal heating, bringing about a distillation. The appearance of the condensation was always noticed by the change in shape of the meniscus. Ethyl ether and glycerine, while serving admirably in every other way for experiment, belong to the second class of substances. The condensation was very rapid as the critical point of ether was approached, and the following very curious effect was noticed. After the critical point had been passed by several degrees, the liquid ether had entirely disappeared in the ether part of the tube, while in the glycerine part of the tube liquid ether still persisted and appeared to be permanent, though no trial was made for a long period of time. The temperature was pushed several degrees higher and all liquid ether disappeared; then the temperature was lowered gradually and liquid ether appeared first in the capillary above the glycerine, then in the outer tube above the glycerine, and finally in the ether tube.

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* Ramsay and Young, Phil. Trans., **178**, 57 (1887).

† Cantor, Wied. Ann., **56**, 493 (1895).

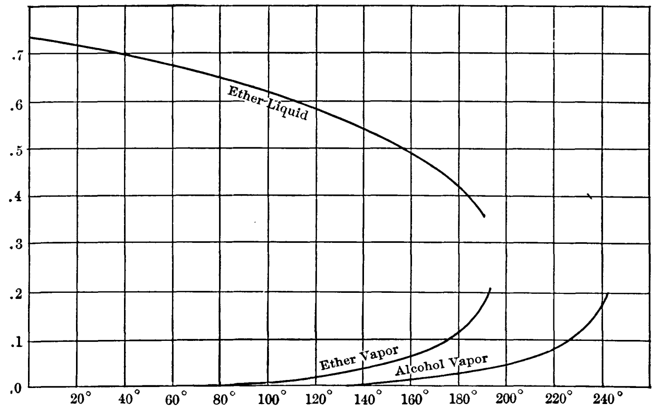

FIGURE 12.

This was interpreted as follows. The effect of Cantor comes first, forming a film of ether on the glycerine surface. Owing to the concavity of this surface, the ether vapor is not in equilibrium with an ether surface at this temperature and is consequently condensed. The presence of a small quantity of glycerine vapor undoubtedly facilitates this condensation. It will be noticed that the capillary tube contains the hottest ether vapor while the whole is cooling off, and here the vapor should condense last. This excludes the possibility of unequal heating being the reason for this effect.

In order to measure the surface tension between liquid glycerine and the vapor of ethyl ether, a special method was employed to keep the temperature of the glycerine above that of the ether so as to avoid the above-mentioned condensation. The glycerine tube was surrounded by a small coil of German silver wire and a separate heating current sent through this. The method of procedure was as follows. When the desired temperature of the heater was obtained, a measured current was sent through this auxiliary coil for a measured time, and then when the condensed liquid had disappeared the current was shut off and measurements taken of the height of the meniscus until the shape of the meniscus changed due to the redeposit of ether. After the completion of the experiments, enough of the tops of the two tubes was removed to insert the two junctions of an iron and German silver thermo-couple. Then the same current that was used previously was sent through the auxiliary coil for the same time and the change in temperature inside the capillary tube measured. Of course the thermo-couple was calibrated by a separate experiment. In this way a rough determination of the rise in temperature was made. It is in error, for the specific heat of ether under such circumstances is unknown. I have used the value for ordinary temperatures.

This temperature of equilibrium between a vapor of one liquid and another liquid has apparently not been studied except by Cantor at room temperature. This will be taken up again by a new method, and instructive results are expected.

Ethyl alcohol and olive oil belong to the first class of liquids, and no precautions were necessary to prevent distillation. Here, however, there is considerable absorption of the vapor by the oil especially at high temperatures. The mixture becomes homogeneous at about 240°.

The alcohol was the purest obtainable and distilled into the tube as described, and the oil was freed from volatile matter by boiling at high temperature.

The following table gives the results of experiments with these substances.

T is the temperature, P the pressure in atmospheres, H the height of the meniscus in cm. (corrected for concavity inside and outside the capillary *), ω the contact angle, $d - d'$ the difference between the densities of olive oil and alcohol vapor, and α the surface tension in dynes per cm.

T	P	H	ω	$d - d'$	α	
°						
12		.594	0	.92	23.2	$r_3 =$ .279 cm.
35		.579	0	.91	22.4	
73	1.18	.519	0	.88	19.4	$r_2 =$ .088 cm.
128	5.48	.367	0	.86	13.3	$r_1 =$ .060 cm.
151	9 88	.308	0	.81	10.4	
176.5	17.7	.234	0	.77	7.5	
201	29.2	.127	0	.75	4.03	
219	41.0	.070	0	.71	2.11	
232	51.4	.040	0	.68	1.16	
241.2	60.3	?	?	.62	?	

Above 232° the meniscus flattened and absorption took place so rapidly that observation was impossible.

Liquid Alcohol and Olive Oil.

An experiment over any considerable range in temperature was impossible with the capillary used, as above 40° the meniscus sunk so low as to be invisible.

At 30.2° the value of α was 14.2 dynes per cm.,† ω being 0 at this temperature although it did not remain so at higher temperatures. r_1, r_2, and r_3 were .348 cm., .102 cm., and .068 cm. respectively.

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* This correction was made by adding $\frac{1}{3} r_1$ and subtracting .11 $(r_3 - r_2)$.

† This is the result of a single experiment.

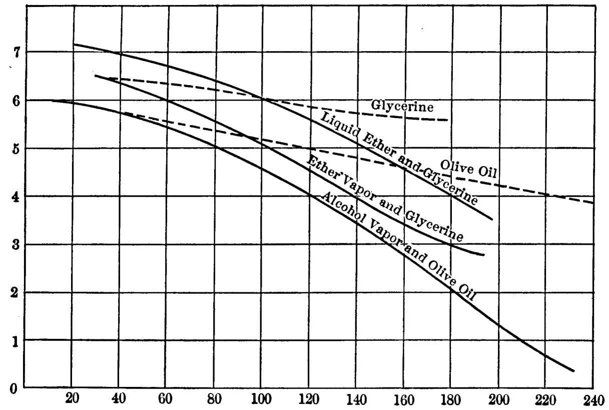

FIGURE 13.

ETHYL ETHER VAPOR AND GLYCERINE.

T	P	H	ω	$d - d'$	a	
°						
31	.86	.645	0	1.25	28 8	$r_3 = .337$
110	7.44	.487	0	1.17	19.7	
120	9.40	.456	0	1.15	18.1	$r_2 = .076$
140.1	14.87	.392	0	1.13	15.3	$r_1 = .056$
150	17.65	.362	0	1.11	13.9	
160.5	21.12	.341	0	1.08	12.7	
170.3	25.17	.315	0	1.05	11.5	
175	27.21	.308	0	1.03	11.0	
185.3	32.94	.300	0	.99	10.3	
193.4	37.19	.288	0	.90	8 7	

T here is the temperature of the heater. $d - d'$ is calculated for the liquid at the temperature of equilibrium, and for the vapor at saturation temperature.

LIQUID ETHYL ETHER AND GLYCERINE.

T °	H	ω	$d - d'$	a	
18.8	.714	17° 25′	.55	15.4	
35.8	.690	no sure change	.55	14.9	$r_3 = .356$
73.2	.617		.56	14.3	$r_2 = .080$
105.8	.586		.59	13.5	$r_1 = .061$
132.3	.526		.63	12.9	
152.3	.470		.65	12.0	
178.0	.418		.71	11.7	
195.6	.350		.80	11.0	
198.8	.345		.82	11.3	
200	.343		.86	11.6	

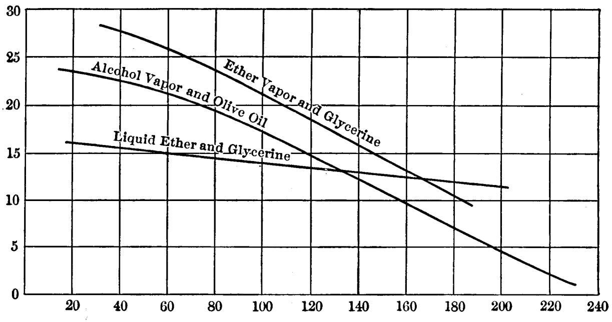

FIGURE 14.

The last two tables show a discrepancy in the value of a not wholly explained. It is probably due to two very large sources of error: 1st, to the impossibility of determining $d - d'$ at temperatures near the normal critical temperature for the liquid-liquid case, and 2d, to the uncertainty concerning the same quantities in the liquid-vapor case, as well as to the fact that a for the latter case is not the value for a true saturated vapor but rather for a superheated vapor.

Figure 13 shows the capillary height plotted as a function of the temperature, the dotted curves showing the height in millimeters when the liquid glycerine and olive oil are in contact with their own vapors, the figures for these results being taken from Weinstein's tables.*

Figure 14 shows the values of α in degrees per cm.

Figure 15 shows the results of the work with the thermopile on the temperature of equilibrium for the case where the vapor condenses on the liquid. Experiments were conducted at temperatures between 132° and 188°. It will be noticed that the equilibrium temperature corresponding to the normal critical temperature is 200°, the temperature at which the meniscus disappeared in the liquid case.

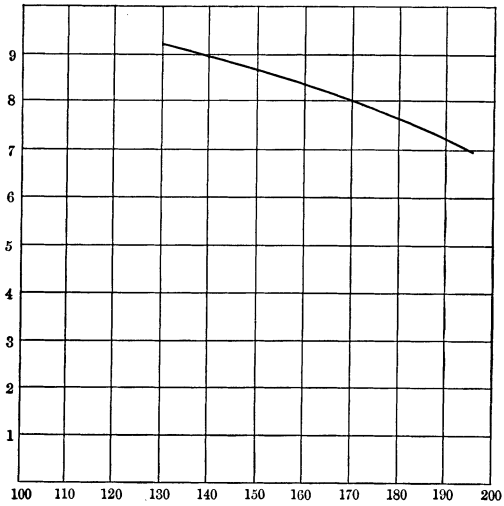

Figure 15.

The curves resemble very closely the curves given by Ramsay and Shields,† showing that the surface tension of a liquid in contact with its own vapor obeys approximately the same laws as for a liquid in contact with the vapor of another liquid.

In closing I wish to extend my heartfelt thanks to the American Academy of Arts and Sciences for their generous appropriation for the apparatus used in the work, to the authorities of Clark University for the opportunity of carrying on the work, and to Professor A. G. Webster for his unfailing kindness and interest.

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* Weinstein, Thermodymik and Kinetik der Körper, Vol. II, p. 49.

† Ramsay and Shields, loc. cit.